

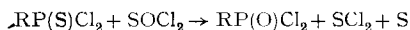
## 42. Organic Phosphorus Compounds 59<sup>1)</sup> A New Method for the Synthesis of Phosphonic Dichlorides [1]

by **Ludwig Maier**

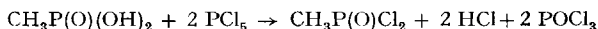
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(20. XII. 72)

*Summary.* Heating of thiophosphonic dichlorides,  $RP(S)Cl_2$ ,  $R = CH_3, C_2H_5, C_6H_5$ , with a molar equivalent of  $SOCl_2$  under pressure at  $150^\circ$  for 5 to 8 h yields phosphonic dichlorides in quantitative yield. In addition sulfur and sulfur dichloride is formed according to the equation:



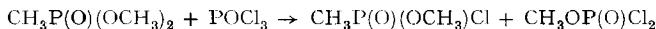
This method is particularly useful for the preparation of  $CH_3P(O)Cl_2$  since it was observed that chlorination of  $CH_3P(O)(OCH_3)_2$  with  $PCl_5$  yields  $CH_3OP(O)Cl_2$  as a by-product which is difficult to separate from  $CH_3P(O)Cl_2$ . On the other hand chlorination of methylphosphonic acid with  $PCl_5$  also gives pure  $CH_3P(O)Cl_2$ .



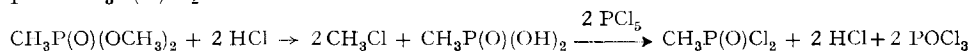
Several methods have been described in the literature for the preparation of phosphonic dichlorides [2]. One of the most widely used procedure consists in the conversion of phosphonates to phosphonic dichlorides by reaction with  $PCl_5$  [2]. This reaction is, however, not as clean as given in the equation:



Often considerable amounts of ester-chlorides,  $RP(O)Cl(OR)$  [3] and other compounds are formed which are difficult to separate from the dichlorides. For example, we observed that when dimethyl-methylphosphonate,  $CH_3P(O)(OCH_3)_2$  was treated with  $PCl_5$  using  $POCl_3$  as solvent, considerable amounts of  $CH_3OP(O)Cl_2$  were formed as by-products which could not be separated by fractional distillation from  $CH_3P(O)Cl_2$ .



We therefore hydrolyzed the phosphonates first to the acid and then chlorinated the acids with  $PCl_5$  to the dichlorides as described in the literature [4]. In this way pure  $CH_3P(O)Cl_2$  was obtained.



Similarly,  $C_2H_5P(O)Cl_2$  was also prepared in this way.

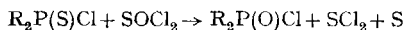
This procedure is, however, somewhat lengthy and troublesome and therefore a simpler method was sought.

Recently, methyl and ethyl-thiophosphonic dichlorides became commercially available<sup>2)</sup>. Therefore attempts were made to convert these thiophosphonic dichlorides in one step to phosphonic chlorides.

<sup>1)</sup> Part 58, sec [1].

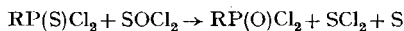
<sup>2)</sup> Ethyl Corporation, Baton Rouge, La.

It is known from the literature [5] [6] that thiophosphinic chlorides may be converted to phosphinic chlorides by reaction with thionyl chloride at reflux temperature (80°). The method was, however, less successful in converting thiophosphonic dichlorides to the corresponding phosphonic dichlorides. Thus heating of PhP(S)Cl<sub>2</sub> with



SOCl<sub>2</sub> for 2 h to 80° (reflux) effected no reaction [6]. Also heating of PSCl<sub>3</sub> with SOCl<sub>2</sub> for 10 h to 80° caused no reaction. And on heating of PhP(S)Cl<sub>2</sub> with SOCl<sub>2</sub> for 10 h to 80° only at 24% conversion to PhP(O)Cl<sub>2</sub> was achieved [6]. We observed that CH<sub>3</sub>P(S)Cl<sub>2</sub> remained unchanged when it was heated with SOCl<sub>2</sub> for 8 h to 80°.

It has now been found that heating of thiophosphonic dichlorides with SOCl<sub>2</sub> to 150° for 5 to 8 h under pressure effects a 100% conversion to the corresponding phosphonic dichlorides. In addition sulfur and sulfur dichloride is formed according to the equation:



Thus when a 1:1.2 mixture of CH<sub>3</sub>P(S)Cl<sub>2</sub> and SOCl<sub>2</sub> was heated in a bomb tube to 150° for 2 h, a product was obtained which consisted of 92 mol-% CH<sub>3</sub>P(O)Cl<sub>2</sub> and 8 mol-% CH<sub>3</sub>P(S)Cl<sub>2</sub>; further heating for 3 h at 150° changed the composition to 98.5 mol-% CH<sub>3</sub>P(O)Cl<sub>2</sub> and 1.5 mol-% CH<sub>3</sub>P(S)Cl<sub>2</sub>; and finally heating for another 3 h effected a 100% conversion to CH<sub>3</sub>P(O)Cl<sub>2</sub>.

This reaction seems to be general. When C<sub>2</sub>H<sub>5</sub>P(S)Cl<sub>2</sub> and PhP(S)Cl<sub>2</sub> were heated with SOCl<sub>2</sub> in a bomb tube to 150° for 5 to 8 h a 100% conversion to the corresponding phosphonic dichlorides was observed.

**Experimental.** – 1. CH<sub>3</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub>(I) and PCl<sub>5</sub> → CH<sub>3</sub>P(O)Cl<sub>2</sub>(II). CH<sub>3</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub> was obtained in 85.3% yield from (CH<sub>3</sub>O)<sub>3</sub>P and a catalytic amount of NaI according to the literature [7], b.p. 70°/11 torr. <sup>1</sup>H-NMR. (in CCl<sub>4</sub>): PCH<sub>3</sub> 1.33 ppm (*d*, J<sub>POCH</sub> 17.7 Hz, 3H), OCH<sub>3</sub> 3.62 ppm (*d*, J<sub>POCH</sub> 11 Hz, 6H); <sup>31</sup>P- 31.5 ppm (in CCl<sub>4</sub>) (Lit. [8] – 32.4 ppm).

A mixture of 116 g (0.93 mol) of CH<sub>3</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub> in 120 ml POCl<sub>3</sub> and 131 g (0.955 mol) of PCl<sub>5</sub> was treated with Cl<sub>2</sub> and then heated to 80–90° as described in the literature [4, p. 388]. Distillation gave a product which contained

CH <sub>3</sub> P(O)Cl <sub>2</sub> :	<sup>31</sup> P- 44.5 ppm; <sup>1</sup> H (in CCl <sub>4</sub> ): 2.48 ppm ( <i>J</i> 16.5). Lit. [9] 2.57 ppm ( <i>J</i> 16.1);
CH <sub>3</sub> P(O)Cl(OCH <sub>3</sub> ):	<sup>31</sup> P- 31 ppm; <sup>1</sup> H: PCH <sub>3</sub> 1.90 ppm ( <i>J</i> 17.5); OCH <sub>3</sub> 3.80 ppm ( <i>J</i> 13.4). Lit. [9] PCH <sub>3</sub> 2.03 ppm ( <i>J</i> 17.4); OCH <sub>3</sub> 3.82 ppm ( <i>J</i> 13.4);
(CH <sub>3</sub> O) <sub>2</sub> P(O)Cl:	<sup>31</sup> P- 6.5 ppm; <sup>1</sup> H: 3.85 ppm ( <i>J</i> 13.5). Lit. [9] 3.87 ppm ( <i>J</i> 13.4);
CH <sub>3</sub> OP(O)Cl <sub>2</sub> :	<sup>31</sup> P- 4.5 ppm; <sup>1</sup> H 4.0 ppm ( <i>J</i> 16.4). Lit. [9] [10] 4.02 ppm ( <i>J</i> 17.1).

Therefore the mixture was treated again with PCl<sub>5</sub> and heated for 2 h to 80°. Fractional distillation gave now a product, b.p. 47.5–50°/10 Torr (84.2 g) which consisted of 75.4 mol-% CH<sub>3</sub>P(O)Cl<sub>2</sub> (<sup>1</sup>H (in CCl<sub>4</sub>): 2.45 ppm (*J*<sub>POCH</sub> 17 Hz) and 24.6 mol-% CH<sub>3</sub>OP(O)Cl<sub>2</sub> (<sup>1</sup>H (in CCl<sub>4</sub>): 3.98 ppm, *J*<sub>POCH</sub> 16.5 Hz) (Lit. [10] 4.08 ppm (in CHCl<sub>3</sub>), *J*<sub>POCH</sub> 16.7 Hz). On standing CH<sub>3</sub>P(O)Cl<sub>2</sub> crystallized out. It was filtered off and found to be pure, m.p. 32°.

2. CH<sub>3</sub>P(O)(OH)<sub>2</sub>(III) and PCl<sub>5</sub> → CH<sub>3</sub>P(O)Cl<sub>2</sub>(II). Hydrolysis of I with conc. HCl at reflux for 14 h gave III in quantitative yield, eq. weight found: 100.12, calc. 96.02. Treatment of 80 g (0.83 mol) III with 430 g (2.07 mol) PCl<sub>5</sub> first at 65–75° then 9 h reflux gave on fractional distillation 238.5 g POCl<sub>3</sub> and 81.2 g (73.5%) CH<sub>3</sub>P(O)Cl<sub>2</sub>, b.p. 34–48°/10 Torr which crystallized on standing to the greater part. <sup>1</sup>H-NMR. (in CCl<sub>4</sub>) indicated that the product is pure II: CH<sub>3</sub> at 2.47 ppm (*J*<sub>POCH</sub> 16.7 Hz); <sup>31</sup>P- 44.5 ppm (Lit. [8] <sup>31</sup>P- 44.5 ppm).

3. C<sub>2</sub>H<sub>5</sub>P(O)(OH)<sub>2</sub>(IV) and SOCl<sub>2</sub> → C<sub>2</sub>H<sub>5</sub>P(O)Cl<sub>2</sub>(V). EtP(O)(OEt)<sub>2</sub> was prepared from (EtO)<sub>3</sub>P and NaI [4], b.p. 75–77°/11 Torr; <sup>1</sup>H-NMR. (in CCl<sub>4</sub>): a) CH<sub>3</sub> 1.28 ppm (*t*); b) PCH<sub>2</sub> 0.94–1.95 ppm (*m*), a + b 10.9 Hz; OCH<sub>2</sub> 4.0 ppm (*J*<sub>HH</sub> 7, *J*<sub>POCH</sub> 8.5 Hz, 4.06 Hz); <sup>31</sup>P- 32 ppm (neat).

Hydrolysis of ethylphosphonate with a 40% solution of HBr gave a quantitative yield of IV as an oily, viscous liquid. Treatment of 79.5 g (0.723 mol) IV with 190 g (1.53 mol)  $\text{SOCl}_2$  at 70° for 3 h, then at 105° until evolution of HCl ceased, gave on distillation 55.5 g (52.8%) V, b.p. 60–61°/10 Torr;  $^1\text{H-NMR}$ . (in  $\text{CCl}_4$ ):  $\text{CH}_3$  at 1.38 ppm (2 t,  $J_{\text{HH}}$  7,  $J_{\text{PCH}}$  30 Hz, 2.99 H);  $\text{CH}_2$  at 2.58 ppm (2 *qu*,  $J_{\text{HH}}$  7,  $J_{\text{PCH}}$  16 Hz, 2.01 H);  $^{31}\text{P}$ - 53.5 ppm (neat) (Lit. [8]  $^{31}\text{P}$ - 53 ppm).

4.  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  and  $\text{SOCl}_2$  at 80°. A mixture of 14.9 g (0.1 mol)  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  and 1.46 g (0.12 mol)  $\text{SOCl}_2$  was refluxed for 8 h at 80°.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR. indicated that after this period no reaction had occurred.  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  was quantitatively recovered by distillation, b.p. 39–43°/0.1 Torr,  $n_{\text{D}}^{20}$  1.5470;  $^1\text{H}$  (in  $\text{CHCl}_3$ ):  $\text{CH}_3$  at 2.78 ppm ( $J_{\text{PCH}}$  14.5 Hz) (Lit. [11] 2.88 ( $J$  14.6 Hz);  $^{31}\text{P}$  –79.5 ppm (neat) (Lit. [8]  $^{31}\text{P}$ - 79.4 ppm).

5.  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  and  $\text{SOCl}_2$  at 150°. Three bomb-tubes were filled each with 10 g (0.067 mol) of  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  and 9.5 g (0.08 mol) of  $\text{SOCl}_2$  and heated in a bomboven to 150°. Tube 1 was removed after 2 h at 150°.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR.-analysis indicated that its content consisted of 92 mol-%  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  [ $^1\text{H-NMR}$ . (in  $\text{CDCl}_3$ ):  $\text{CH}_3$  at 2.28 ppm ( $J_{\text{PCH}}$  16.4 Hz),  $^{31}\text{P}$ - 44 ppm] and 8 mol-%  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$  [ $^1\text{H-NMR}$ . (in  $\text{CDCl}_3$ ):  $\text{CH}_3$  at 2.78 ppm ( $J_{\text{PCH}}$  14.8 Hz)  $^{31}\text{P}$ - 80 ppm].

In addition a trace of  $\text{POCl}_3$  was seen in the  $^{31}\text{P}$ -NMR. at –3.5 ppm.

Tube 2 was removed after 5 h at 150°.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR. analysis indicated that the solution consisted of 98.6 mol-%  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  and 1.4 mol-%  $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ .

Tube 3 was removed after 8 h at 150°.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR.-analysis indicated that the solution consisted of a 100 mol-%  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ . Distillation of the contents of each tube gave  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  b.p. 53–54°/10 Torr, m.p. 30–32° and  $\text{SCL}_2$ ; in addition crystalline sulfur was isolated.

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6.  $\text{C}_2\text{H}_5\overset{\text{S}}{\text{P}}\text{Cl}_2 + \text{SOCl}_2$  at 150°. A bomb tube was filled with 20 g of  $\text{C}_2\text{H}_5\text{P}(\text{S})\text{Cl}_2$  (0.123 mol) and 17.6 g (0.148 mol) of  $\text{SOCl}_2$  and heated for 5 h to 150°. After this period a dark violet solution was present and crystalline sulfur had precipitated.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR.-analysis indicated that  $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$  was formed in a 100% conversion. Distillation gave pure  $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$  b.p. 33°/3 Torr, 75–78°/50 Torr.  $^1\text{H-NMR}$ . (in  $\text{CDCl}_3$ ):  $\text{CH}_3$  at 1.4 ppm (2 t,  $J_{\text{HH}}$  7.5,  $J_{\text{PCH}}$  30 Hz, 3H);  $\text{CH}_2$  at 2.5 ppm (2 *qu*,  $J_{\text{HH}}$  7.5,  $J_{\text{PCH}}$  14.5 Hz, 2H),  $^{31}\text{P}$ - 54 ppm (neat); contains a trace of  $\text{P}(\text{O})\text{Cl}_3$  at –3.5 ppm (must have been formed by a P–C bond cleavage.)

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7.  $\text{C}_6\text{H}_5\overset{\text{S}}{\text{P}}\text{Cl}_2 + \text{SOCl}_2$  at 150°. A bomb tube was filled with 20 g (0.095 mol)  $\text{PhP}(\text{S})\text{Cl}_2$  and 13.6 g (0.114 mol)  $\text{SOCl}_2$  and heated in a bomb oven to 150° for 5 h. A yellow solution is obtained which consist, according to  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR.-analysis, of 82 mol-%  $\text{PhP}(\text{O})\text{Cl}_2$  ( $^{31}\text{P}$ - 34 ppm) and 18 mol-%  $\text{PhP}(\text{S})\text{Cl}_2$  ( $^{31}\text{P}$ - 74.5 ppm) (Lit. [8] – 34 ppm and –74.8 ppm, respectively).

Another tube filled with the same amounts of reagents was heated for 8 h to 150°. Thereby a quantitative conversion to  $\text{PhP}(\text{O})\text{Cl}_2$  was effected. Distillation gave  $\text{SCL}_2$  and  $\text{PhP}(\text{O})\text{Cl}_2$ , b.p. 104°/4 Torr;  $^{31}\text{P}$ - 34 ppm (neat);  $^1\text{H-NMR}$ . (in  $\text{CDCl}_3$ ): *m*- and *p*-CH 7.65 (*m*, 3H); *o*-CH 8.06 (*m*, 2H).

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